WORKSHOP ON

REMOTE SENSING OF VOLCANIC GASES: CURRENT STATUS AND FUTURE DIRECTIONS

Honolulu, Hawaii
26-27 February 1979

A Workshop co-sponsored by the
LUNAR AND PLANETARY INSTITUTE
and the
UNIVERSITY OF HAWAII

UNIVERSITIES SPACE RESEARCH ASSOCIATION
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WORKSHOP ON

REMOTE SENSING OF VOLCANIC GASES: CURRENT STATUS AND FUTURE DIRECTIONS

CONVENERS:

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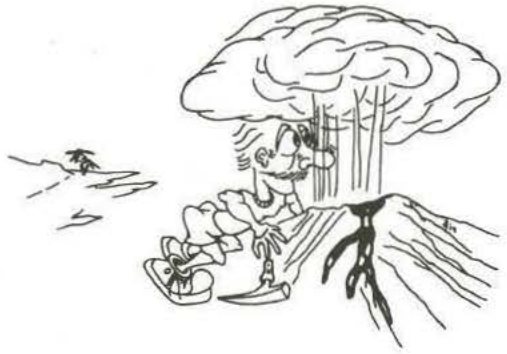

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LPI Contribution 368

INTRODUCTION

This volume contains abstracts of talks presented at a Workshop on Remote Sensing of Volcanic Gases: Current Status and Future Directions held at the University of Hawaii on 26-27 February 1979. The volume begins with a summary prepared by the conveners, Thomas R. McGetchin (Lunar and Planetary Institute) and Thomas B. McCord (University of Hawaii) and ends with a bibliography of volcanic gases and remote sensing.

Logistic support was provided by Carolyn Kohring of the LPI and Sandra Ostrowski of the University of Hawaii. This volume was compiled by Carolyn Kohring.

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Lunar and Planetary Institute
Houston, Texas
May 1979

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Summary of Workshop
on
Remote Sensing of Volcanic Gases

LPI and U. Hawaii

26–27 Feb. 1979

Compiled by

Tom McGetchin and Tom McCord

based on the contributions and

discussion of all the participants

1. Background and Rationale

There appears to be potential for substantial improvement in our knowledge of the volcanic contribution of gases to the earth's atmosphere by (1) application of existing technology and (2) development of new methods, especially in remote sensing. It appears that strong impetus to pursue development of new methods exists because of the possibility of (1) important climatic effects of volcanic effluents (both chemical and particulate), (2) the potential use of individual eruptions as "tracers" in studies of global atmospheric chemistry and physics, (3) volcanic hazards and the need for eruption prediction, (4) applications to planetary exploration, which will have as a focal point during the next decade volcanism on other planets (e.g., Venus, Mars, Io), and (5) the coming availability of earth orbit platforms through Shuttle.

2. The Workshop and Participants

On February 26 and 27, 1979, 16 scientists met at the University of Hawaii (1) to review the current state of knowledge of volcanic gases, the methods previously used and the principal scientific questions upon which these data bear, and (2) to discuss the most important directions for future research, both extensions of existing activities and new direction, in terms of instrumentation, sites, coordinated activities, and new or different modes of remote sensing such as from space or in drill holes.

3. Definition of Principal Scientific Problems and Desired Solutions

Volcanic gases bear upon a number of important scientific problems; among the more prominent are:

Volatile Budget of the Earth. We need to determine the present and past fluxes (gross and net) of the principal volatile species from/to the earth's interior. The abundances within the principal resources and fluxes between them must be evaluated. These bear on our understanding of the outgassing of the earth and, as some scientists now believe, the loss of a selective part of atmosphere to the interior by subduction.

The Origin of Planetary Atmospheres. The bulk composition of planets is commonly related to elemental abundances in meteorites. We need to know the composition of the earth's mantle (and core), how it varied with time, depth and temperature, and how the earth's atmosphere relates to these internal changes. Differences among the planets (as revealed by recently returned spacecraft measurements of Venus, Mars and the Galilean satellites) relate both to the process of formation within the early solar nebula and also to their subsequent thermal evolution. The evolution of planetary atmospheres is linked to the interiors, at least in part; we must understand the volcanic processes which deliver atmospheric gas to the surface (and perhaps subtract them) if we hope to understand planetary atmospheres in general.

Volatiles in Magma. The behavior and chemical evolution of batches of magma are *dominated* by the abundance and character of the volatiles present. For example, it is now known from experimental petrology that completely different differentiation trends result in basalts produced from

partial melting of peridotite systems which differ only in volatile composition (CO_2 vs H_2O). Hence volatiles in magmas are crucial to our understanding of chemical evolution of lavas and the behavior of volcanoes.

Eruption Prediction/Effects and Hazard Assessment. For individual volcanoes which are near heavily populated areas and which therefore are potentially dangerous, we need to know several basic things about eruptions; namely, is an eruption likely or possible? If so, *when, where, how big* and specifically what are the effects likely to be? We need sufficient experience (an observational data base extending over a sufficiently long time and number of cases) to use observed changes reliably to predict the future course of events. *Beyond* this, we need theoretical models which use observational data to predict changes. This implies and requires a much deeper understanding than empirical relationships and correlations can give.

Climatic Effects. How does the output of volcanoes (gas and particulate material) affect climate, on both the long and short time scale? Is it important relative to other effects such as man-made changes (industrial CO_2, deforestation, SST exhaust, chemical rocket-Shuttle operations)? We know clusters of eruptions (in the 1880's) have serious global effects. Why and how? What would their effects be now?

Atmospheric Dynamics/Global Circulation. Individual eruptions place large amounts of gas and particulate matter into the atmosphere; about once per year an eruption penetrates the tropopause and places these products into the stratosphere where it is carried world-wide. These events serve as small scale perturbations on the global atmosphere system; the products serve as natural "tracers". What are the important species? How do they behave? Why?

Global Biology. How do gases (particularly toxic ones) behave in the dynamic interface between the atmosphere and the surface? What is the natural background of toxic substances (such as mercury) and what are the natural secular changes? What are the sources, sinks, fluxes and abundances (such as the global volatile budget discussed above)?

In each of these areas there are important specific questions to ask, (1) What *is* the problem — is there a model context in which questions can be asked? (2) What are the key observable parameters; what's missing from the data base? How good are the available data? (3) What existing methods and approaches are likely to yield important results? (4) What *new* methods are likely to be important? (5) What can (or should) be done next? What recommendations should be made to sources of potential research funding?

4. Status of Research

4.1 Data Base — Previous Work

A variety of gas analysis techniques has been applied at Kilauea (see Table 1); these represent reasonably well methods used elsewhere. Several problems have plagued volcanic gas collection methods (Gerlach), namely: inclusion of atmospheric gases, addition of

Table 1. A review of the status of remote and/or *in situ* continuous monitors for volcanic gas studies.

WHAT	WHO	HOW	PRESENT STATUS	WHERE
1) H_2 (IC)	M. Sato (USGS)	Fuel cell	E (since '73)	Hawaii, Iceland Italy, Mt. Baker
2) He (IC)	Irv Friedman (USGS)	Mass spect.	E, D	Yellowstone (Hawaii)
3) HCl (R)	R. Stoiber (Dartmouth)	Correlation spectrometer	E, D	----
4) HF (IC)	USGS-HVO	Selective ion electrode	B	(Hawaii)
5) H_2S	----	PbAc strip	D	(Hawaii)
6) SO_2 (R)	R. Stoiber French (CNRS-CEA)	Correlation spectrometer	X	Etna, Central America, Hawaii
7) CO_2 (R) (IC)	J. Naughton(HIG) M. Sato (USGS)	I.R. electrode	E D	Hawaii
8) Hg (IC)	----	Thin gold film	D, B	----

R = remote
IC = *in situ* with continuous transmission

X = routine
E = experimental
D = developmental
B = drawing board

References (does not include Japanese or Russian literature).

1) H_2 — Sato *et al.*, (1976) E@S 59, (abs.).

2) He — *

3) HCl — No published reference.

4) HF — No published reference.

5) H_2S — *

6) SO_2 — Numerous abstracts by Stoiber; several French articles; See MS thesis by L.L. Malinconico Jr., 1978, Dartmouth College.

7) CO_2 — Naughton et al. (1969) J. Geophys. Res. 74, 3273-3277.

8) Hg — *

* Various publications contain details of measurement techniques as applied to pollution monitoring. No known references to volcanic applications.

This table was provided by T. J. Casadevall, USGS, Hawaiian Volcano Observatory.

meteoric water, condensation-reevaporation (S and H_2O), reaction between erupted gases and container, oxidation of minor species, incomplete chemical analyses and analytical errors. Data from high-temperature fumaroles have contributed the best results to date; such collections need to be continued and extended to more silicic volcanoes. Also laboratory work on glass inclusions in volcanic rocks (which yield volatiles) and fluid inclusion studies are providing important data (e.g., F. Anderson; Delaney).

Best available estimates (Gerlach, Thomas, Naughton) show (a) that H_2O and CO_2 constitute 80 to 90% (molar) of volcanic gases in basaltic systems; (b) they are somewhat reduced in that H_2, CO, and H_2S are present, totaling several percent; and (c) SO_2 varies greatly and depends strongly on oxidation-reduction conditions in the melt (sulfur-poor gases are characteristic of reduced melts).

The problem of differentiating between juvenile volatiles and recycled surface volatiles is most effectively addressed using isotopic studies, particularly H/D, C^{13}/C^{12} and oxygen isotopes (Thomas).

To date, remote sensing for general gas abundance studies has been experimental. Grating spectrometers, IR-emission and absorption observations have revealed H_2O, CO_2 and SO_2 (Naughton).

The problem of separating the atmospheric from volcanic plume constituents has not been solved. Volcanic flame (emission) spectroscopy (Cruikshank) has shown features (in the region of 6700 Å) caused by combustion of hydrogen in air. SO_2, however has been determined remotely in Central America and at Kilauea using long path infrared spectroscopy (see Stoiber). Similar methods, plus direct collection on airborne filters are used in studies of atmospheric aerosols — principally sulfur and halogens. The matrix attached summarizes work at Kilauea to date on various methods of gas analysis.

An important distinction needs to be made between remote sensing and telemetry of data taken *in situ*. There have been attempts to do both. Peter Ward's experiment in the early 1970's is an important example of the latter: 15 active volcanoes in Alaska, Hawaii and Central America were instrumented with seismic event counters and monitored over the course of about a year, utilizing satellite communication. Their principal problems were with *telemetry*, specifically antennas. Hence, the challenge is to do simple things reliably before elaborate measurements are attempted.

4.2 Some Other Interesting Results

Some particularly interesting results were reported by participants and are listed below:

Hydrogen Abundance in Fumaroles Prior to Eruptions (Casadevall). Fumarole probes in Iceland and Hawaii indicate that hydrogen abundance increases are well correlated with increased seismicity. Both are associated with emplacement of new batches of melt, hence the technique (of Sato) is believed to have potential for eruption prediction.

Radioactive Species and Radon (Le Guern). Radioactive species of Pb, Po and Bi may be released from the surface of fresh lava (magma); increases of these species (when normalized to radon) are believed to indicate fresh lava near the surface, hence may be important in eruption prediction.

Sulfur Oxidation State (Gerlach). The total sulfur content of volcanic gases associated with mafic lavas appears to vary with the oxygen fugacity of the melt. Sulfur-rich gases are characteristic of relatively oxidized melts, while sulphur-poor gases are commonly associated with more reduced melts.

Negative Outgassing During Subduction/Sulfur (Decker). The classical view of Rubey and Goldschmidt suggests that planetary atmospheres are outgassed (probably continuously) from volcanoes. Fyfe and Hargraves have suggested recently that the opposite may be true, namely as subduction proceeds some volatiles may be irreversibly introduced into the interior; sulfur could have been "scrubbed" from the Earth's surface in this way, where as on Venus it was not.

Methane Associated With Igneous Activity (Gerlach). Carbon and hydrogen of the gas phase associated with basaltic magma at low pressures and high temperatures is present mainly as CO_2 and H_2O; at subsolidus conditions during cooling at depth, substantial amounts of CH_4 are possible. This may account for methane associated with the East African Rift and also some alkaline plutons.

Mercury (Siegel, *et al.*). Plants play a key role in the transfer between the atmosphere and the earth's interior. Studies of background and bio-geochemistry must be done before the geochemical cycle of many toxic elements can be defined.

Gas and Fluid Inclusion Studies (Gibson). Recent developments in analytical methods and the presence of glass and fluid inclusions in many volcanic rocks indicate that this is a fruitful research direction to pursue; the ion probe and gas release studies should provide important new results.

Lidar Methods (Discussion). The return signal from a vertically oriented pulsed ruby laser (624 nm) has been used to determine the abundance and distribution of atmosphere aerosols.

Equilibrium-Disequilibrium (Gerlach). Short-term changes in gas compositions (in basaltic volcanoes) appear to be very small; longer term variations are larger and mainly related to changes in CO_2 content.

Gas Release Studies (Gibson). Gas chromatography and mass spectrometry utilizing gas released by stepwise heating up to melting temperatures have been applied to some volcanic rocks in addition to lunar samples and meteorites. Extremely low sensitivities are routinely obtained (ppb-range for many species); the techniques should be applied more vigorously to volcanic problems.

Kilauea Gas Studies (Thomas, Naughton). The principal gases observed are H_2O, CO_2, and SO_2; air and groundwater are admixed with juvenile species in all samples. Variations are observed in both time and position; short time variations are believed to be due primarily to contamination by air and ground. Isotopic studies (C, He) suggest substantial fractionations between the magma reservoir and fumarole, hence volatiles which escape may account for only a small part of the budget. If so, surface ratios may vary from those at the source.

5. Conclusions

The present data base on volcanic gases is inadequate to address the principal scientific problems of interest in a satisfactory way. However, we believe that substantial progress is possible if the following things are done:

- Continue to make field collections of *high temperature gases* from fumaroles. These provide the best available data. Extension of observations from basaltic to more silicic volcanoes is important.

- Continue and expand laboratory studies on *volatiles in rocks*. Studies of volatiles in glass inclusions and from fluid inclusions are yielding important new results. These studies need to be encouraged. Also, studies of deep seat xenoliths should be included. Coordinated (consortia) approaches to those problems (similar to those in the lunar program) should be encouraged.

- Expand theoretical and laboratory studies of silicate melt-volatile equilibria; solubilities as functions of P and T are crucial to understanding processes and/or interpreting data.

- Monitoring of 10 to 20 active volcanoes on a decade scale is essential to provide the necessary experience (three to five eruptions) to *begin* to address eruption prediction properly. There was a strong consensus that it is crucial to establish a steady stream of reliable data. Simple measurements with very reliable telemetry are required for seismicity, tilt or ground deformation, fumarole gas chemistry and temperature, in addition to routine surveillence methods from orbit.

- Intensive field studies of volcanoes prior to and during eruption are essential, well coordinated, carefully-preplanned studies of eruptions by *small experienced* teams and are much more likely to yield good results than larger efforts by part-time investigators which respond to crisis situations.

- Deep drill holes into volcanoes were discussed and there was disagreement about their effectiveness. Some felt the environment would be so unstable that practical problems would override potential gains; others felt there would be potentially great gains made by getting below surface disturbances of several types of volcanoes.

- The vantage point of *space* may prove most effective as a communication link (between *in situ* experiments at widely separated sites and a data collection center), rather than for direct remote sensing. (A data collection site in Hawaii could serve as such a center for the entire Pacific Basin utilizing one equatorial geosynchrous satellite.)

- Theoretical studies of the thermochemistry of gas systems, of the physics and chemistry of volcanic systems and processes, and of tectonic processes as they relate to volcanoes and gases, should be *closely tied* to observational and laboratory experimental programs as a part of integrated research groups and through meetings and workshops.

- Coordination between volcanological research groups within the U.S. (among government agencies and labs, and the university community) and internationally (through scientific organizations such as IAV) must be improved. (Hawaii's location within the Pacific Basin provides an excellent opportunity to serve as a focus for work around the entire circumPacific margin.)

- Continue to apply results from terrestrial studies to analysis of results from previous planetary missions, particularly the comparison of the atmospheres of Mars, Venus, and the Earth. It is equally important to the long-term program to integrate the results into the planning of the next generation of flight missions, especially to problems of analysis of possible active volcanism on Mars, Venus and Io through instrumentation of their volcanoes by means similar to those described above for the Earth.

There was a strong consensus that improvements are possible in several modes:

If funds are tight, doing simple things *well*, in the field, and increasing cooperation and communication among scientists already active in the field will yield modest but quite significant progress.

If an ambitious program of volcano science develops, then a program of volcano monitoring involving both new and existing technology, utilizing space communications and platforms to intensively study 10 to

20 sites and providing for a moderate but well focused supporting R & D program in theoretical and laboratory studies, could produce revolutionary results in terms of (a) volcano eruption prediction, (b) our understanding of volcanoes as physical and chemical systems, (c) the volatile budget of the earth *in the context* of a dynamically convecting interior – the plate tectonics view, and (d) our understanding of how planetary atmospheres and interiors evolve. These results would be scientifically substantial and exciting, and would contribute to problems in mineral resources (volcanogenic ore deposits), energy resources (geothermal energy), and in future planetary exploration.

Workshop on
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CURRENT STATUS AND FUTURE DIRECTIONS

PROGRAM

Room 310
Campus Center
University of Hawaii

Monday, 26 February 1979

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Tom McGetchin and Tom McCord

Overview
Fraser Fanale

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Chemical and Isotopic Variations Observed in the Fumarole Discharges of Kilauea Volcano
Don Thomas

Evaluation of Volcanic Gas Analyses from Tholeiitic and Alkaline Mafic Lavas
Terry Gerlach

Volatiles in Lunar and Terrestrial Rocks
Everett Gibson

METHODS PREVIOUSLY STUDIED

Field Observations of Volcanic Gases at Erta Ale, Kilauea, and Marape
Francois LeGuern

H_2O Monitoring (with Sato input); SO_2 Monitoring (with Stoiber input)
Tom Casadevall

Volcanic Gas Collection and Remote Sensing Experience on Hawaiian Volcanoes by the Hawaii Institute of Geophysics
John Naughton

Tuesday, 27 February 1979

SPECTROSCOPY OF GASES AND APPLICATIONS

Volcanic Gases: Hydrogen Burning at Kilauea Volcano, Hawaii
Dale Cruikshank

Mercury and Antarctic Volcanism: I) A Comparative Aerometric Study; II) Anomalous Distribution Between Atmospheres and Substratum; III) The Biotic Connection
Sanford Siegel, Barbara Siegel, Gary McMurthy and R. Brill

CURRENT STATUS OF VOLCANO MONITORING

Excess Volatiles Reconsidered
Bob Decker

DISCUSSION OF FUTURE RESEARCH DIRECTIONS

Instrumentation and Methods

Sites

Relative Merits of Ground-based, Bore-hole, Aircraft and Space-craft Measurements

Planetary Applications — Mars, Venus

Workshop on

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MERCURY AND ANTARCTIC VOLCANISM I. A COMPARATIVE AEROMETRIC STUDY

R. Brill, G. McMurtry, B. Z. Siegel and S. M. Siegel. University of Hawaii, Honolulu, Hawaii., 96822

Atmospheric measurements carried out during the Austral Summer of 1978-79 on Mt. Erebus, and in the McMurdo area generally, (fig.1) show that Antarctic air mercury levels are of the same magnitude as those previously found in Iceland and Hawaii, and contain similar proportions of elemental vapor, Hg° (table 1).

Table 1 Air Mercury in Three Volcanic Regions

	$\mu g \cdot m^{-3}$	% Hg°
Iceland (36 samples)		
Thermal Areas	9.4 ± 4.4	28
Non-thermal Areas	0.8 ± 0.2	--
Hawaii (*ca* 220 samples)		
Thermal Areas	17.4 ± 3.4	36
Non-thermal Areas	1.1 ± 0.5	--
Antarctica (32 samples)		
General	8.2 ± 1.4	40

Fig. 1 1978-79 Sample site in Antarctica. x, McMurdo; y, Weddel Sea; o = South Pole.

An examination of air Hg near fumerolic sources in Hawaii Volcanoes National Park shows that over the period 1971-78 although the values ranged from 2.3 to 28.5 $\mu g \cdot m^{-3}$, the Hg° varied between 13.5 and 31.5% of the total.

Other locations on Kilauea are also similar in Hg° content although variable in total Hg. In the more extreme cases, for example during the late stages of the 1977 eruption, sampling up to 1100 m over fume areas showed Hg° to increase with altitude. Compared with often cited baselines of 0.003-0.03 $\mu g \cdot m^{-3}$ for open sea air, levels of 0.84-1.35 $\mu g \cdot m^{-3}$ were found over the 380 km interisland corridor from Hawaii to Oahu at altitudes of 1000-2500 m above m.s.l., whereas measurements at 3000 m over the Weddel Sea (20 Dec. 78) some 3500 km NNE of Mt. Erebus reached nearly 22 $\mu g \cdot m^{-3}$, 68% Hg°; and 1000 m over S. Pole Station (27 Dec. 78), nearly halfway between Erebus and the Weddel Sea the Hg totalled 3.3 $\mu g \cdot m^{-3}$, 30% Hg°. These compare with the Erebus plume measurement at 3794 m (23 Dec. 78) of *ca* 14 $\mu g \cdot m^{-3}$, 64% Hg°.

Evidence for human disturbance was obtained at McMurdo Station itself in proximity to leaky fuel containers and the "town dump". (table 2)

Table 2 Effect of Wind Conditions on Hg Composition of McMurdo Air

Date	Wind	Area: Jet fuel Storage		Area: Scott Base	
		$\mu g \cdot m^{-3}$	% Hg	$\mu g \cdot m^{-3}$	% Hg
31. XII. 78	Variable 0-7 kn	97.7	0.6	160.4	2.1
7. I. 79	N-NE 30-35 kn	13.2	34	0.74	27

Overall, these data show that high levels of Hg emission and high proportions of Hg° are characteristic of widely separated volcanic systems of diverse origin and chemistry.

Work carried out under NSF Grant Division of Polar Programs 77-21507.

VOLCANIC GASES: HYDROGEN BURNING AT KILAUEA VOLCANO, HAWAII. Dale P. Cruikshank, David Morrison, Institute for Astronomy, University of Hawaii, Honolulu, Hawaii 96822, and Kenneth Lennon, Department of Chemistry, University of Hawaii, Honolulu, Hawaii 96822.

Spectroscopic evidence for hydrogen burning in air was obtained at Kilauea Volcano. The abundance of hydrogen required to support combustion is consistent with that predicted for gases in equilibrium with typical Hawaiian tholeiitic basalt.

Abstract from paper, "Volcanic Gases: Hydrogen Burning at Kilauea Volcano, Hawaii," Science 182, 277-279 (1973). Please see journal for complete paper.

EXCESS VOLATILES RECONSIDERED. Robert W. Decker, Hawaiian Volcano Observatory, U. S. Geological Survey, Hawaii National Park, HI 96718 and James G. Moore, U. S. Geological Survey, Menlo Park, CA

William Rubey in 1951 proposed that the volatile constituents of the atmosphere, oceans, and sedimentary rocks, which could not have been reasonably derived from rock weathering, originate by outgassing of the earth's interior and are largely of volcanic origin. The principal excess volatiles (H_2O, C, Cl, N, S) can now be considered more quantitatively with newer data on the chemistry of submarine lavas in which the gases have been trapped, and on the rates of generation of mid-ocean ridge volcanic and shallow intrusive rocks. Present rates of generation of carbon and nitrogen are in good agreement with a steady-state plate tectonic model of atmospheric and oceanic formation. Present rates of water and chlorine generation are too low by a factor of 2 to 4. Present rate of sulfur generation is too high by a factor of 50.

This paper was originally presented at the IASPEI/IAVCEI Assembly in Durham, England, August, 1977.

SEMI-ULTIMATE QUESTIONS. F. P. Fanale, Space Science Division, Jet Propulsion Laboratory, Pasadena, CA 91104

1. If a large volume of natural thoelitic/olivine basalt or dunitic melts is equilibrated at its solidus in an inert closed crucible with its own gas (at low pressure) in a very small dead space, what would the composition of that gas be? At high pressure?

   a) theoretical calculation

   b) experimental observation

   c) what is explanation of any discrepancies between a & b?

2. If an imaginary membrane were place around the solid surface of the earth today, what would be the flux, the molecular composition and (more importantly) the mass balance of the volatiles that could be seen to pass from the interior to the atmosphere and sediment system?

3. If the flux of volatiles returning to the solid surface via oceanic deposition, subduction of geosynclinal sediments, oxidation of igneous rocks (the exospheric H flux to space should be considered here) were also monitored, what would that flux and mass balance be?

4. If you subtract "3" from "2", what is the net genuine contributory flux of additional volatiles currently supplied to the atmosphere and sediment (+ space - for H) system?

5. Is the mass balance or general composition of either the gross flux in "2" or the net flux in "4" explicable in terms of the composition of basaltic or ultramafic rocks using the kinds of thermodynamic calculations (presumably based on Fe^{+2}/Fe^{+3} ratios, melting points, etc.) and experimental observations (presumably involving the best rock gas and top one percentile of volcanic gas analyses available)? What are relative roles of mantle vs. crustal buffers?

6. Where does this gas come from? That is, are fumaroles and hot springs 100 times as important as volcanoes or not? Would the answer be different depending on whether one "counted" both the recycled flux (as in "3") and the so-called "genuine" flux (in "4") vs. "counting" only the "genuine" or "net" influx?

7. What subtleties are involved in the precise mechanisms of release or transport to the surface that influence either the molecular composition or the net mass balance of volatiles?

   Examples: a) H_2 preferential diffusion from magma chambers-how does this affect the major preceeding questions ultimately?

   b) Are there relic pressure effects to be seen in "bubble gas" in rocks or in naturally effused gas?

SEMI-ULTIMATE QUESTIONS

F. P. Fanale

c) body diffusion from earth as whole?

8. What happens to "rock gas" (which includes recycled gas and genuine juvenile gas, but which does not include casually admixed or reacted air components) when it effuses from volcanoes or other sources? Can you trace it as a plume which is gradually being degraded by spatial spreading, photodissociation, etc.? What changes (e.g. oxidation) take place at the atmosphere/magma interface or even within the magma?

9. In answering "8", what results or developmental techniques can you draw on from studies of the geochemical fate of stack pollutant plumes which have been made using airborne remote sensing techniques and groundbased observations?

10. What can be done to understand the flux of volatiles from the 3/5 of the earth that is covered by oceans (presumably since the ^4He flux is comparable on continental and oceanic areas — as is the heat flow — the general volatile is as well)?

11. What new experimental techniques can be utilized to elucidate the above problems?

a) airborne spectroscopic (rotational?)

b) groundbased sampling of gases from vents using new techniques

c) rock gas studies (new Raman or Laser techniques? new ways to avoid wall effects or to simulate natural release?)

12. What theoretical studies would be useful in understanding volatile supply to the Earth's surface?

a) calculation of equilibrium compositon of magmatic gas as it exists in the magma chamber

b) calculation of the chemical history (equilibrium plus kinetic considerations) of magmatic gas as it bleeds out into the surface environment.

c) calculation of the chemical history of magmatic gas as it cools (equilibrium plus kinetic considerations) in bubbles in a rock.

13. How can you relate your data to pertinent isotopic data and what does the latter data tell you about volcanic gas history?

14. Is the assumption implied that equilibration between gas and rock generally ceases to be effective below the solidus — correct? How does this interact with preferential H diffusion?

15. In general, is the assumption that rock chemistry controls fO_2 and other critical parameters correct? That is, if a carbonate bed was plowed under at a continental margin, would it merely contribute C atoms to a molecular composition the CO_2:CO ratio of which was entirely overwhelmed by the sea of new magmatic rock

SEMI-ULTIMATE QUESTIONS

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involved?

16. How has the answer to all these questions varied with time? Can one say that there exists a present mantle buffer or crustal buffer that, in the end, controls fO_2, hence the mass balance? Was it the same 2 billion years ago? How is the answer reflected in Fe^2/Fe^3 for basaltic rock of different ages? What about fO_2, mass balance, etc. for the volatile flux in early history 3.5 billion years?

17. Nomenclature: How (if at all) should the following terms be used: rock gas, juvenile gas, magmatic gas, volcanic gas, etc.? What is an H_2O molecule that was introduced to a magma chamber by rain and then re-emitted as steam? What is a CO_2 molecule in volcanic gas that was derived from subducted carbonate sediments?

18. Does most gas being supplied to the earth's surface come out of either fumaroles or volcanoes or any other local source or does most of it ooze out ubiquitously? How can we relate the juvenile gas flux to, say, the ^4He flux or the heat flux?

19. What is special about the capabilities of remote sensing techniques based from a) field stations, b) low altitude observations, c) high altitude observations, and d) orbit which may allow them to be used more effectively to shed light on the above questions that other techniques?

20. Do any of these techniques have any early warning potential as civil defense systems as well as scientific tools?

EVALUATION OF VOLCANIC GAS ANALYSES FROM THOLEIITIC AND ALKALINE MAFIC LAVAS:* T. M. Gerlach, Sandia Laboratories**, Albuquerque, New Mexico 87185

There are approximately 100 volcanic gas analyses of collections taken at high temperatures (>950°C) in source regions of tholeiitic and alkaline mafic lavas (Hawaii, 1918-19; Nyiragongo, 1959; Surtsey, 1964-67; Etna, 1970; Erta Ale, 1971-74). These "high quality" volcanic gas samples exhibit erratic chemical characteristics. Atmospheric contamination has long been recognized as an obvious cause of much of the observed variability, however substantial compositional variation remains even after the analyses have been corrected for air contamination. This feature has compromised attempts by volcanologists to relate the collections in terms of temporal, spatial and petrologic parameters.

Detailed computerized studies of the "high quality" gas samples have led to an identification of several sources of modification in addition to atmospheric contamination. These include: addition of meteoric H_2O; condensation and re-evaporation of S and H_2O in lead-in tubes; reactions between the erupted gases and metal sampling equipment; oxidation of minor species (S_2, H_2S, H_2, CO); incomplete chemical analyses; and analytical errors in H_2O determinations. Reduced gases tend to result when samples are collected in metal sample bottles (e.g., Etna, 1970). Samples taken with evacuated glass tubes have frequently become oxidized (e.g., Erta Ale, 1971). The least modified samples are those taken in glass sample bottles connected to metal lead-in tubes (Surtsey, 1964-67 and Erta Ale, 1974). Most techniques have provided little or no direct information on HCl, HF, H_2S, S_2 and COS.

The author has developed procedures for correcting the reported analyses for several of the imposed modifications noted above. The restored analyses are believed to be representative of the erupted gases. The principal species in all the restored analyses are H_2O, CO_2 and SO_2. Minor species include H_2, CO, H_2S, S_2 and HCl; the latter three are rarely observed directly, but are usually inferred from condensate analyses and thermodynamic calculations. Minor amounts of N_2 and A are also present. Trace species, which repeatedly occur in the restored compositions, but which are rarely reported in the analyses, are COS, SO, S_2O and HS. Trace amounts of CH_4 can be present in high temperature volcanic gases, but high concentrations as well as the presence of higher hydrocarbons and organohalogens (e.g., CH_3Cl), suggests contamination by pyrolysis of organic materials.

The restored analyses provide a basis for several interesting observations and inferences:

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**A DOE Facility.

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(1) Volcanic gases are erupted in a state closely approaching chemical equilibrium.

(2) After removal of imposed modifications, apparent short-term variations (minutes-hours) virtually disappear, implying that meaningful data can be obtained over relatively short periods of observation.

(3) Long-term variations (months-years) are apparent in some series of collections after the scatter imposed by secondary variations is removed. Evidence of long-term variations consists mainly of decreasing CO_2 content with time--a trend compatible with the lower solubility of CO_2 relative to H_2O and S in silicate melts.

(4) The restored analyses of gases collected from tholeiitic lavas in regions of crustal spreading (e.g., Surtsey and Erta Ale) are characterized by high H_2O contents (70-90 mole %). Those from alkaline lavas are characterized by lower H_2O (45-50 mole %) and relatively high CO_2 (25-50 mole %). These observations are consistent with recent experimental evidence on the effects of volatile compositions on the chemistry of partial melts formed under mantle conditions.

(5) The total sulfur content (SO_2, S_2, H_2S) of volcanic gases appears to be in part a function of the O_2 partial pressure of the outgassing lava. Relatively reduced lavas (e.g., Surtsey and Nyiragongo) produce gases with low total sulfur (1-3 mole %). More oxidized lavas (e.g., Etna) contain up to 30 mole % total sulfur. The direct relationship between O_2 partial pressure and sulfur outgassing of lavas has a simple thermodynamic explanation and can be shown to be pressure dependent. These observations may have considerable bearing on the atmospheric and climatologic effects of volcanic outgassing.

EVALUATION OF VOLCANIC GAS ANALYSES

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MOLE %

VOLCANO	H_2O	H_2	CO_2	CO	SO_2	S_2	H_2S
ERTA ALE (1971)	70.	1.6	17.8	.8	9.	.5	1.
ERTA ALE (1973)	71.	2.1	19.4	1.2	4.9	.3	.8
ERTA ALE (1974)	77.	1.6	11.7	.5	7.4	.3	.9
SURTSEY (1964)	82.	2.8	9.8	.7	3.2	.1	.7
SURTSEY (1965)	88.	2.3	6.4	.4	2.4	.05	.3
SURTSEY (1967)	91.-92.	1.4-1.8	1.-3.	.7	2.8-3.7	.02	.12
MOUNT ETNA (1970)							
1	47.	.5	23.	.5	29.	.3	.2
2	48.	.5	20.	.4	30.	.3	.2
3	49.	.5	34.	.7	15.	.1	.1
NYIRANGONGO (1959)	44.-56.	1.3-2.2	49.-36.	2.2	2.-1.	.6-.4	1.7-2.5

VOLATILES IN LUNAR AND TERRESTRIAL ROCKS. Everett K. Gibson[1], SN7 Geochemistry Branch, NASA Johnson Space Center, Houston, TX 77058 ([1]Present Address: Earth Sciences Division, National Science Foundation, Washington, D. C. 20550).

The origins, states, abundances, and distributions of the volatile elements and compounds in terrestrial and extraterrestrial materials must be accurately measured and interpreted. The mineralogical-petrological relationships between the inorganic and organic phases must be understood. Eventually, the geochemical cycles for the volatile elements (H, C, N, O, S etc.) must be determined. A complete understanding of the role of volatiles will assist in elucidating the physical and chemical processes acting at the surface-atmosphere interface.

The analytical tools available for volatile studies include specific analyzers (e.g. H_2O or H_2 probes), multiple component analyzers (e.g. G. C. or mass spectrometers) or combination techniques (G.C.-M.S., Pyrolysis-mass spectrometry/or G.C.). No matter which analytical techniques are used, selection of suitable samples for analysis must be done with extreme care. In the case of volcanic gases, the samples analyzed must be the best possible sample which would represent the primary gas phase. Distinguishing between representative and non-representative gases from the primary source from secondary gases must be accomplished.

During the past decade our laboratory has developed various analytical methods for analysis of volatiles in terrestrial and extraterrestrial materials. Pyrolysis-mass spectrometry, infrared analysis along with specific element and compound analyzers have been used as separate or combined analytical tools for analyzing the volatiles in lunar samples, meteorites, basalts and planetary surface analogs. The pyrolysis-mass spectrometry method has been used to distinguish between the different forms of volatiles in samples (e.g. adsorbed gases, low temperature minerals, gases trapped within vesicles and/or microinclusions, reaction products produced at elevated temperatures, etc.) (1). Crushing-gas chromatography methods have been developed for the accurate analysis of gases trapped within phenocrysts and/or glass samples of terrestrial and lunar basalts (2). Recent studies (3) of separated glass and phenocrysts from an Apollo 12 vitrophyre have shown the presence of CO and N_2 trapped within the sample. The results are the first experimental measurements of the possible "original" lunar magmatic gases. The detection of CO and N_2 within these samples confirms theoretical gas-phase equilibrium calculations of Wellman (4), Gerlach (5) and Sato (6).

Sulfur abundances measured in lunar and terrestrial basalts have shown that lunar basalts have up to ten times more sulfur that terrestrial subaerial basalts (7). It appears that the source regions for the lunar basalts are enriched in sulfur as compared to their terrestrial equivalent. Submarine basalts, which contain the greatest sulfur concentrations observed in terrestrial basalts, are depleted in sulfur by factors of two to four as compared to lunar basalts. Carbon abundances for fresh terrestrial basalts are greater by a factor of two to ten than lunar basalts. Lunar basalts typically contain less than 20 μg C/g whereas terrestrial basalts usually contain carbon abundances greater than 100 μg C/g (8). The planetary question which must be answered is: "Why are lunar basalts enriched in sulfur but depleted in carbon relative to terrestrial basalts?"

VOLATILES IN LUNAR AND TERRESTRIAL ROCKS

E. K. Gibson

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FIELD MEASUREMENTS OF VOLCANIC GASES. F. Le Guern. Laboratoire de Volcanologie, CFR CNRS, 91190 Gif/Yvette, France.

A field gas chromatograph built in 1978 was used in the field analyse volcanic gases befor the water vapor condensation. Tested in Vulcano (Italy), Kilauea (Hawaii) and Merapi (Indonesia) this technique provides the actual composition of the volcanic gas mixture. We thus observed the mixture of H_2S and SO_2 in fumarolic and high temperature magmatic gases (up to 819°C).

The major components of volcanic gases are H_2O: 70 to 99% and in decreasing concentrations: CO_2, SO_2, H_2S, CO, COS, CH_4, HCL, HF, Halogens, metallic salts and rare earth. The study of volcanic eruptions used in forcast, geothermal research, ore deposits and volcanic contribution to the atmosphere and hydrosphere needs techniques of collection and analysis that does not transform the composition of the gas phase.

Different techniques were tested in high temperature magmatic gases:

In 1963 Naughton collected the gases on silicagel adsorbant columns: desorbtion and analysis were made in the laboratory. This technique stopping the molecular reactions provides a gas composition representative of the sample, but the analysis took a long time in the laboratory (Naughton et al., 1963).

In 1969 Tazieff, Elskens and Tonani tested a field gas chromatograph on the Italian volcanoes. That system measured in continuous the CO_2 partial pressure in the volcanic gases. The other gases were condensed in a cool trap and analysed in the laboratory (Elskens et al., 1969).

In 1978 Le Guern, Bicocchi, Nohl and Tazieff elaborated a field gas chromatograph. The volcanic gases are cooled in a Silica tube, and the analyses are made in the field at 130°C in a two column automatic gas chromatograph. With that new technique we completely avoid the corrosion and the change in the molecular composition. Oven column and detector are fixed in a 12x12cm cylinder. The prototype weight 12 Kg; power and carrier gas can be carried in the field by 3 persons and can work one week without providing new equipment (Le Guern, 1979).

The results obtained during the 1978 field work are summarized in Table 1 where we compare the classic techniques of collection in sampling preevacuated flasks with dehydrating P_2O_5 and the field gas chromatograph. We can make some constatations:

The complete analysis is obtained in the field in 20 minutes.

With that technique we have the minimum atmospherical contamination.

Water content is obtained in the field before condensation in dry vapor.

If we consider the sample Merapi 1978 at 720°C we can write the following equilibrium (after Matsuo, 1962):

(1) $2H_2S + SO_2 \rightleftarrows 3/2\ S_2\ gas + 2H_2O$

(2) $H_2S + 2H_2O \rightleftarrows 3H_2 + SO_2$

FIELD MEASUREMENTS OF VOLCANIC GASES

F. Le Guern

$$(3)\quad \log K_1 = \frac{-1494}{T} - 0.78 + 1.38 \log T - 6.11 \times 10^{-4} T + 8 \times 10^{-8} T^2$$

$$(4)\quad \text{where} \quad K_1 = \frac{[S_2]^{3/2}\,[H_2O]^2}{[H_2S]^2\,[SO_2]}$$

$$(5)\quad \log K_2 = \frac{-10414}{T} - 5.45 + 2.82 \log T + 5.24 \times 10^{-4} T - 3.28 \times 10^{-7} T^2 + 4.9 \times 10^{11} T^3$$

$$(6)\quad \text{where} \quad K_2 = \frac{[H_2]^3\,[SO_2]}{[H_2O]^2\,[H_2S]}$$

We can calculate K_2 from the analysed molecular composition. We obtain T graphically in (6) and use T in (3) to calculate S_2. The equilibrium temperature obtained is 879°C and the S_2 content 1.53×10^{-2} mole %. The sulfur gas content is very low and all the sulfur is $H_2S + SO_2$. The ratio $H_2S/SO_2=1$ gives a temperature of equilibrium very close to the collection temperature. Calculated and observed molecular compositions are in good agreement. This technique prevents sulfur molecular reactions.

With the techniques usually operated in the filed with the preevacuated glass bottles, cooling and water vapor condensation change the molecular composition.

We consider the equilibrium:

$$(7)\quad 2H_2S + SO_2 \rightleftarrows 3S \text{ gas} + 2H_2O \text{ gas}$$

and the reaction:

$$(8)\quad 2H_2S + SO_2 \rightleftarrows 3S \text{ solid} + 2H_2O \text{ liquid}$$

During the collection the temperature of the gases decrease under the melting point of sulfur (113°C for rhombic sulfur). The equilibrium (7) of high temperature breacks down and the reaction (9) start working until the total depletion of the less concentrated sulfur molecule on the left side of the equilibrium. After that first step we reach a second step that is the water condensation and the oxydation of SO_2 in SO_3 and H_2SO_4. Operating at 130°C the field gas chromatograph prevents all these transformations.

Conclusion. With this new technique:

We obtain in the field the molecular composition including the water content in 20 minutes; we operate fast enough to survey and forcast.

FIELD MEASUREMENTS OF VOLCANIC GASES

F. Le Guern

We have observed the mixture of SO_2 and H_2S in fumarolic and magmatic gases from andesitic volcanoes during rich Pb, Zn, Cu... sublimates collections into the silica tubes we are now able to reconsider experimentally the ore deposits.

Correlating this new technique with SO_2 remote sensing we shall be able to make a budget of the volcanic contribution to the atmosphere for the species analysed.

This technique can provide instant measurements of the gas composition during a drilling in a geothermal field (as in Kilauea Iki in February 1979).

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Table 1. Results obtained with the field gas chromatograph.

DATE	LOCATION	TEMPERATURE IN °C	TECHNIQUE	CONCENTRATION IN MOLES %								
				H_2	CH_4	CO	CO_2	H_2S	SO_2	O_2+Ar	N_2	H_2O
1978	KIL 1	95	Sam.		0.005		16		11	0.04	0.4	non. anal
1978	KIL 1	95	Sam. dehy.		0.3		16	0.03	11	0.04	0.3	non. anal
1978	KIL 1	95	Field		0.005		15	0.09	13	0.004	0.02	72
1979	KIL 1	93	Sam. dehy.		0.08		64		25	1.83	8.9	non. anal
1979	KIL 1	93	Field	0.03	0.55		31	0.11	11	0.004	0.19	56.7
1979	KIL 1		Field plume				6.15		2.4	18.79	72.63	non. anal
1979	KIL 1		Field plume				3.22		0.9	20.22	75.65	non. anal
1979	KIL 1		Field plume				2.96		0.6	20.73	75.65	non. anal
1979	KIL IKI	870-97	Field				0.003	0.009	0.17		0.17	99.65
1978	VUL	220	Sam.				21		0.7	0.03	0.3	non. anal
1978	VUL	220	Field				20	0.6	1.17	0.004	0.01	78
1977	MER	710	Sam.	0.37	0.0007	0.2	3.5		0.11	0.04	0.6	95
1978	MER	720	Field	1.36	0.017	0.03	4.0	0.3	0.31	0.19	0.68	93
1978	MER	819	Field	0.5	0.01	0.01	4.6	0.5	0.51	0.005	0.1	94
LOWEST DETECTABLE CONCENTRATION:				0.3	0.004	0.014	0.004	0.01	0.01	0.004	0.005	0.02

Sam. = Samples collected in preevacuated bottles.
Sam. dehy. = Samples collected in preevacuated bottles dehydrated with P_2O_5.
Field = Field measurements with the gas chromatograph operating in the fumarolle.
Field plume = Field measurements with the gas chromatograph operating in the plume.
KIL 1 = Kilauea Hawaii, 1971 eruptive fissure, area of strong sulfur deposition, location of hydrogen gas probe and popular gas sampling site for visiting chemists.
KIL IKI = Measurements made in the 1979 drill hole; reached molten lava at 175 feet.
VUL = Vulcano Island (Italy) hottest fumarolle in the crater.
MER = Merapi (Indonesia) gases from fumarolles near the active Dome with glowing avalanches activity.

Table 2. A review of the status of French volcanic gas studies.

WHAT	WHO	HOW	PRESENT STATUS	WHERE
Radon 222, ^{210}Pb, ^{210}Bi ^{210}Po	Lambert Polian Bristeau CFR Gif/Yvette 91190 France	Aerosols collection counting in the field; counting in the lab.	X,D	Etna, Erebus, Merapi, Vulcano, Hawaii
HCl, HF, S, SO_2, H_2S	Faivre Pierret LESI 85X38041 Grenoble France	preimpregnated filters	X	Etna, Erebus, Telica, Masaya, Momotombo, Merapi, Hawaii
Si, P, S, Cl, K, Ca, Ti, V, Mn, Fe, Cu, Zn, As, Se, Br, Sr, Au, Pb, Bi, Hg,...	Darzi, Florida State University Vie le Sage Univ. Paris	Impactors Strikers	X X	Etna, Vulcano, Hawaii
H_2, H_2S, SO_2, COS, CO, CH_4, H_2O	Le Guern CFR CNRS 91190 Gif/Yvette France	Field gas chromatograph with thermal conductivity detector	X	Vulcano, Merapi, Hawaii
H_2, CH_4, COS	Le Guern	Field gas chromatograph; flame ionisation detector	D,B	
Halogen trace elements	Le Guern CFR CRNS	Silica tubes to collect with continuous temperature recording during collection	X,D	Etna, Vulcano, Merapi, Hawaii
Heath flow measurements	Carbonndelle Le Guern	Infra red telescope	X,D	Reunion Isl., Nyiragongo, Erta Ale, Vulcano

X = routine
D = developmental
B = drawing board

The first six studies are in situ measurements; the last is remote sensing.

MERCURY AND ANTARCTIC VOLCANISM II. ANOMALOUS DISTRIBUTION BETWEEN ATMOSPHERE AND SUBSTRATUM. G. McMurtry, R. Brill, B. Z. Siegel and S. M. Siegel. University of Hawaii, Honolulu, Hawaii 96822

Some nine years of sample collection and analysis in Iceland (fig. 1) and Hawaii (fig. 2) have produced a picture of consistent air-soil mercury relations. Excluding extremes of meteorology and topography, the Hg content of local soils or other substrata reflects the Hg level of the local atmosphere. In SW Iceland, representative levels at Geysir; at Hekla; at the Krysuvik thermal area or the Reykjanes peninsula, and at Surtsey are 6 to 37 $\mu g \cdot m^{-3}$. Representative soil Hg values range up to 400 $\mu g \cdot kg^{-1}$. In contrast in the far west and far east air values of 1 $\mu g \cdot m^{-3}$ are common and soils fall to extreme low readings of 3-5 $\mu g \cdot kg^{-1}$. The same situation obtains on the Island of Hawaii, where the Kilauea-East Rift air levels of 10-79 $\mu g \cdot m^{-3}$ are associated with mean soil figures of 100-1900 $\mu g \cdot kg^{-1}$ (but reaching 40,000 $\mu g \cdot kg^{-1}$ in some localized areas). Again, air values elsewhere of 1 $\mu g \cdot m^{-3}$ or less are associated with lower soil levels.

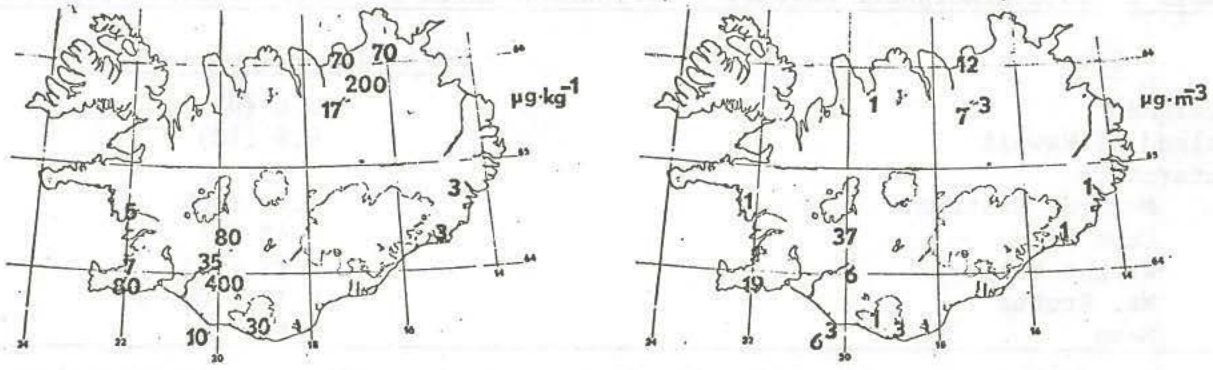

Fig. 1 Soil (left) and Air (right) Hg levels in Iceland. Data collected 1970-75.

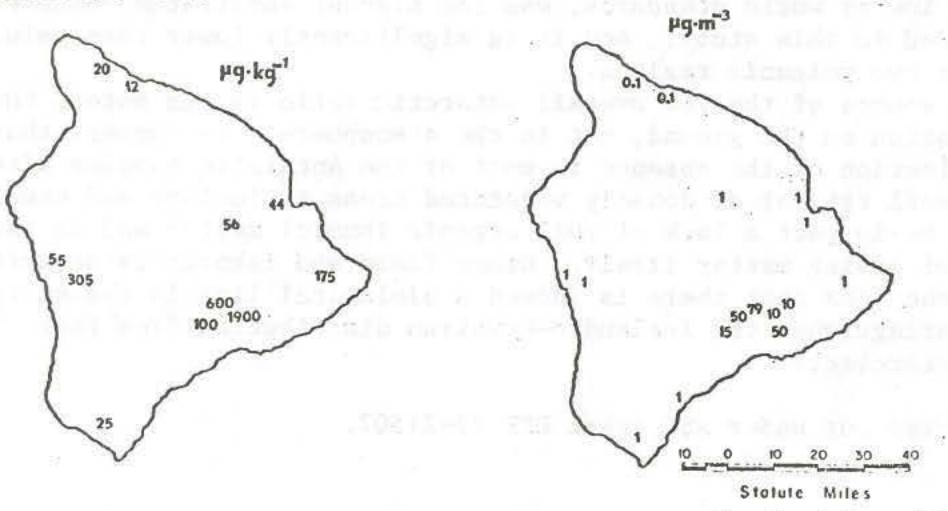

Fig. 2 Soil (left) and Air (right) Hg levels on the Island of Hawaii. Data collected 1970-78.

Following acquisition of air sample data at levels to be expected in volcanic regions, the results of substratum analysis were unexpected (table 1) as they showed a consistent low value compared with a mean crustal abundance of 50 $\mu g \cdot kg^{-1}$.

Table 1 Mercury Contents of Substratum Solids at Antarctic Collection Sites

Location	Samples	Mean Hg Content $\mu g \cdot kg^{-1}$
McMurdo Station	15: muds and fines	7.1 ± 5.6
Cape Bird	4: ash	2.0 ± 0.8
Wright Valley (at DJ Pond)	16: evaporites, sediments, muds, morraine sands	3.1 ± 1.2
Mt. Erebus	11: ash, tephras, basalts	1.2 ± 1.0

The nature of the anomalous "soil-air" relationship is evident when values of *ca* 7-10 for Iceland and Hawaii are compared with four Antarctic stations (table 2).

Table 2 Soil-Atmosphere Mercury Distribution Ratio in Three Volcanic Regions

Site	Soil Hg/Atmospheric Hg
Iceland	10.8 (9)
Island of Hawaii	6.8 (18)
Antarctica	
McMurdo Station	1.78 (10)
Cape Bird	0.48 (4)
Wright Valley	0.29 (10)
Mt. Erebus	0.14 (10)
Mean	0.67

The only Antarctic location displaying a ratio equal to or greater than unity was at McMurdo Station, where the "soil" Hg level of 7 $\mu g \cdot kg^{-1}$, although low by world standards, was the highest substratum concentration encountered in this study. And it is significantly lower than values for the other two volcanic regions.

The source of the low overall Antarctic ratio is, as noted, the low Hg concentration on the ground, not in the atmosphere. We suggest that this is a reflection of the absence in most of the Antarctic samples sites of a genuine soil typical of densely vegetated areas in Iceland and Hawaii. This may be in part a lack of soil organic (humic) matter and in part a low density of living matter itself. Other field and laboratory activities support the idea that there is indeed a biological link in the Hg cycle which distinguishes the Icelandic-Hawaiian distribution from that observed in the Antarctic.

Work carried out under NSF Grant DPP 77-21507.

VOLCANIC GAS COLLECTION AND REMOTE SENSING EXPERIENCE ON HAWAIIAN VOLCANOES BY THE HAWAII INSTITUTE OF GEOPHYSICS GROUP. John J. Naughton, Chem. Dept. and Hawaii Inst. of Geophysics, U. of Hawaii, Honolulu, HI 96822.

The classic collections of volcanic gases at Kilauea and Mauna Loa on Hawaii by T. A. Jaggar, and the analyses of these gases by E. S. Shepherd, have supplied earth scientists with data which has been exhaustively interpreted [1]. Ellis [2] pointed out that volcanic volatile mixtures might be regarded as equilibrium systems, and this has provided the impetus for most recent studies.

Methods of direct gas collection first used in Hawaii were (a) the "pump-through" method of pulling gases into a glass bulb by means of a suction pump, followed by isolation of the gas in the bulb when a satisfactory sample had been obtained, and (b) the "vacuum bulb" method of drawing a sample into a previously evacuated bulb by fracture of a fragile break-off tip, followed by sealing the bulb by means of a stopcock or sealing wax [1]. Most investigators were aware that interactions of the gases occurred during and after collection, and that the collected gas mixture did not truly represent the composition of the gases within the vent.

To prevent these interactions an evacuated glass or silica tube was developed which contained a column of activated silica gel in the inlet tube [3]. This separated the active gases as layers in the silica gel column (a chromatographic effect), and retained them in a close-to-primary equilibrium condition. After sampling, the tubes were sealed by means of a portable glass-blowing torch, or temporarily sealed with a teflon stopper and later fused. Subsequently the sampling tube arrangement was modified by placing the tubes within larger silica tubes and filling the intervening space with thermal insulation (silica wool, alumina pellets, or diatomaceous earth) [4]. The insulated tubes could be introduced into hot vents and drill holes with temperatures up to 1100°C, with remote manipulation and opening by means of wires. The whole collecting operation could be accomplished in about one minute without the temperature of the inner sampling tube exceeding 100°C (when the gases separated on the silica gel would start to desorb and react).

For analysis, the sampling tubes were attached to a gas chromatograph and the adsorbed gas driven off by controlled heating of the tube in a suitable furnace [3]. It is believed that improved insulation and larger protecting tubes would enable these chromatographic type samplers to be lowered into primary vents under certain conditions to enable sampling of gas just as it is released from the source lava. Similar arrangements have been used successfully to sample volcanic condensates [5].

Remote sensing of gases being evolved at lava fountains has been attempted by measurement of the optical absorption in the

infrared (2-14 μ, or 4000-650 cm^{-1}) [6]. This could be done most effectively by alternately focussing a small IR scanner to the top of the lava fountain (gas present), and near the base (gas minimal or absent), ideally during steady fountaining conditions with little wind disturbance. The incandescent lava was the IR source. Many repeated sweeps were necessary to average small fountain condition variations. H_2O, CO_2 and SO_2, the major component of magmatic gas, can be measured by this technique. From the measured composition of the major atomic components from these sources (H, O, C and S), the composition of the minor components can be calculated using equilibrium theory [7].

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MERCURY AND ANTARCTIC VOLCANISM III. THE BIOTIC CONNECTION.
B. Siegel, S. Siegel, G. McMurtry, and R. Brill. University of Hawaii, Honolulu, Hawaii 96822

The mean ratio Soil Hg/Air Hg was 10.8 for nine Icelandic stations and 6.8 for 18 sample sites on the Island of Hawaii, but only 0.67 for 34 sites at Mt. Erebus and nearby Antarctic locations including Ross Island and the dry valleys. Air mercury values are comparable to those in Iceland and Hawaii, but are associated with surprisingly low substratum levels for a volcanic region, hence a ratio which is less than unity. We suggest that this relationship arises from the scarcity of biota, especially vegetation, and organic derivatives common to tropical, tundra and boreal soils. Alternatively, the capability for concentrating Hg from the environment and re-emitting it to the atmosphere after sometime may be attenuated in Antarctic organisms.

In Iceland, Hawaii and Alaska, 60% of 239 vascular plant-soil sample sets yielded Hg bio-concentration indices of 2 to 10-fold or more. High accumulation factors are also common for algae and aquatic organisms but most mosses and lichens fall into the range 1-2.

A comparison of various aquatic forms (table 1) shows that the Antarctic species sampled, although not in the extreme range of Icelandic and Hawaiian accumulations, are fully capable of concentrating ambient Hg.

Table 1 Mercury Accumulation in Aquatic Organisms

Sample	Hg Content ($\mu g \cdot kg^{-1}$)	Ratio (organism/water)
	A. Antarctic	
Ulva	1.5	8.3
Echinoids	21-33	117-183
Crustaceans	37	206
Octopods	3	17
Antarctic cod (Dissostichus)		
Whole	36	200
Blood	52	288
	B. Hawaii	
Sargassum	26-46	12-23
Padina	140-185	65-88
Ulva	48-220	25-145
Echinoids	380-500	190-250
Marlin (Makaira)	>500	>250
Tuna (Neothunnus)	220-1370	110-685
	C. Iceland	
Cladophora	106	1060
Potamogeton	12	120
Mastigocladus	380	3800
Trout (Salmo)	287	2870

This capability is further shown in dry valley algal mats (table 2) and seabird feathers.

The humid tropics (e.g. Hawaii) commonly support phytomass densities of 50-70 $kg \cdot m^{-2}$ whereas the boreal range in Iceland falls to *ca* 6-35 $kg \cdot m^{-2}$ and the Arctic to *ca* 0.5-2.8 $kg \cdot m^{-2}$. In contrast, the concentrated algal mat at Don Juan Pond (Wright Valley) is itself only 0.2 $kg \cdot m^{-2}$ and if averaged over the area studied, must be orders of magnitude smaller. We conclude that it is indeed the low holding capacity of the Antarctic

surface that distinguishes this region, and that vegetation-dominated biogeochemical cycling, including massive accumulation and re-emission into the atmosphere (Fig. 1) is of marginal significance at best.

Table 2 Algal Mat Mercury Accumulation

A. Don Juan Pond (Wright Valley)

Specimen	Mercury Content $\mu g \cdot kg^{-1}$
Brine	3.40
Stream water	0.25
Sediments	3.1 (7)
Evaporites	2.8 (6)
Algal mat	10.6 (2)

B. Hoare Lake (Taylor Valley)

Level	Mercury Content $\mu g \cdot kg^{-1}(al^{-1})$
Sediments (*ca* 2-3 cm depth)	1.6 (4)
Water below algal mat	<0.1
Algal mat	19.4
Water above algal mat	<0.1

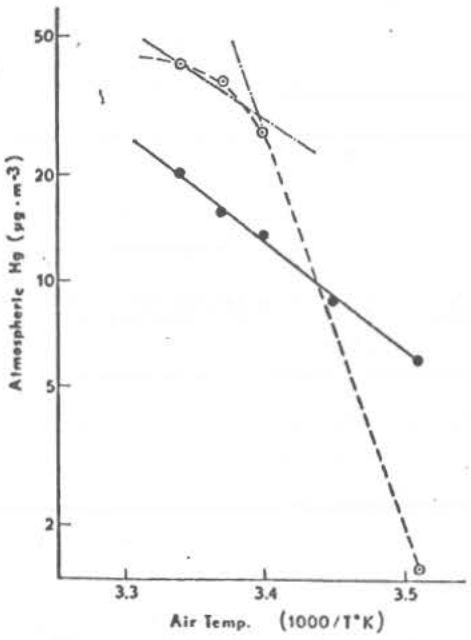

Fig. 1 Arrhenius plot of Air Hg vs. temperature at the air-soil interface (dashed curve) compared with P_{vapor} for Hg at the same temperatures.

Work carried out under NSF Grant DPP 77-21507.

CHEMICAL AND ISOTOPIC VARIATIONS OBSERVED IN THE FUMAROLE DISCHARGES OF KILAUEA VOLCANO. Donald M. Thomas, Hawaii Institute of Geophysics, University of Hawaii, Honolulu, Hawaii 96822.

The chemical and isotopic composition of the gases from several Kilauea summit fumaroles have been monitored over a period of several years. During these observations several important aspects of the fumarolic emissions have been observed:

1) There are widely divergent gas compositions in fumaroles which may be separated by only short distances.

2) Temporal changes take place in the relative ratios of the major and minor components of the emissions which occur on time scales ranging from several minutes to several weeks.

3) The isotopic compositions of carbon and helium obtained from the summit fumaroles, while similar, appear to exhibit fractionation effects resulting from their migration to the surface.

4) Short-time scale variations also appear to be present which probably result from near surface environmental influences.

The data obtained during the period of observation have led to the following conclusions:

a) The chemical compositions and temperature of the fumarolic emissions are strongly dependent upon access of atmospheric gases and groundwaters to the migration routes of the fumarolic gases.

b) Substantial fractions of the volatiles released from the summit magma reservoir are undoubtedly lost from the fumarole conduits prior to their arrival at the surface (i.e. the surface emissions of volcanic and fumarole gases may account for only a small fraction of total magmatic volatile budget).

c) The isotopic ratio obtained for magmatic volatiles from fumarole emissions probably differs substantially from both those present in the abyssal sources as well as those for the total volatile mass entering the near surface environment.

VARIATIONS OBSERVED IN FUMAROLE DISCHARGES — KILAUEA

D. M. Thomas

CARBON DIOXIDE ISOTOPE RATIOS

Sample Location	Date	$\delta^{13}C$ vs. PDB
Sulphur Bank	08/05/75 #1	-3.19
	08/05/75 #2	-2.62
	08/18/75	-3.43
	11/08/75 #1	-2.29
	11/08/75 #2	-3.24
	12/75 #1	-3.01
	12/75 #2	-2.54
	08/13/76	-3.42
	08/17/76	-3.37
	10/13/76 #1	-3.61
	10/13/76 #2	-3.01
	12/01/76	-2.68
	12/28/76	-3.51
	01/28/77	-3.3

$\delta^{13}C$ $\bar{X}$ =-3.09 S = 0.41

Sample Location	Date	$\delta^{13}C$ vs. PDB
1971 Fissure	08/13/75	-3.35
	08/19/75	-3.21
	11/08/75	-3.29
	12/01/75 #1	-3.19
	12/01/75 #2	-3.31
	08/09/76 #1	-3.18
	08/09/76 #2	-3.28
	08/26/76	-3.41
	10/13/76	-3.50

VARIATIONS OBSERVED IN FUMAROLE DISCHARGES — KILAUEA

D. M. Thomas

Sample Location	Date	$\delta^{13}C$ vs. PDB
1971 Fissure (cont.)	12/01/76	-3.19
	12/29/76	-3.57
	01/29/77	-3.4
	$\delta^{13}C\ \bar{X}$ =-3.32	S = 0.13

CARBON DIOXIDE ISOTOPE RATIOS

Sample Location	Date	$\delta^{13}C$ vs. PDB
1974 Fissure	01/29/77	-3.13
	02/10/77	-2.95
1974 Fissure	$^{13}C\ \bar{X}$ = -3.04	
Kilauea Iki	08/76	-15.73
	11/09/76	-11.57
	02/10/77	- 8.59
Hualalai Olivine		- 10.3
		- 13.4
		- 12.1
		- 14.0
		$\delta^{13}C\ X$ = -12.5

Gas Compositions* for Kilauea Summit Fumaroles

		O_2	N_2	He x 10^4	H_2	CO_2	SO_2	H_2S	T (°C)
Sulphur Bank	10/31/76	0.026	3.2	19	--	97	-0-	--	97
	12/10/76	0.41	2.4	2.2	--	96	1.5	--	
1971 Fissure	01/20/77	--	0.36	9.6	--	74.5	25.2	--	145
	04/06/77	0.07	2.8	20	--	91	6.5	--	
1974 Fissure	01/29/77	12.7	51.8	3.3	--	35.5	--	--	97
Kilauea Iki	01/29/77		16.0	--	78	6	--	tr.	
Sulphur Bank**	01/21/60	0.08	6.6	--	0.001	86	5.7	1.8	
Kilauea Iki**	07/27/60	19.2	73.1	--	7.5	.15	0.02		

*Concentrations are in mole percent (excluding water vapor).

**Heald et al., 1963.

$^3He/^4He$ Ratios for Kilauea Summit and Flank

Sample Location	Date	Total Helium cm^3 STP	$^3He/^4He$	Comments
Sulphur Bank	8/5/76	$2.35\pm0.03\times10^{-3}$	$1.992\pm0.008\times10^{-5}$	Pyrex sample tube
Sulphur Bank	8/18/76	$2.87\pm0.03\times10^{-3}$	$1.940\pm0.008\times10^{-5}$	Pyrex sample tube
Sulphur Bank	12/1/76	$3.49\pm0.03\times10^{-3}$	$1.952\pm0.008\times10^{-5}$	Pyrex sample tube
Sulphur Bank	1/28/77	$8.49\pm0.03\times10^{-7}$	$1.770\pm0.008\times10^{-5}$	Copper sample tube
1971 Fissure	8/13/76	†$5.\pm2 \times10^{-3}$	$1.8\pm0.2 \times10^{-5}$	Pyrex sample tube
1971 Fissure	8/13/76	$2.83\pm0.03\times10^{-3}$	$1.941\pm0.008\times10^{-5}$	Pyrex sample tube
1971 Fissure	12/1/76	$3.97\pm0.03\times10^{-3}$	$1.850\pm0.008\times10^{-5}$	Pyrex sample tube
1971 Fissure	1/29/77	$7.25\pm0.03\times10^{-5}$	$1.860\pm0.008\times10^{-5}$	Copper sample tube
1974 Fissure	1/29/77	$7.31\pm0.03\times10^{-5}$	$1.290\pm0.008\times10^{-5}$	Copper sample tube
HGP-A 3500 ft	1/25/77	†$>>6 \times10^{-6}$	$>>8.25 \times10^{-6}$	Copper sample tube
HGP-A 5800 ft	1/25/77	$3.20\pm0.03\times10^{-6}$	$8.250\pm0.008\times10^{-6}$	Copper sample tube
HGP-A	2/9/77	$2.69\pm0.03\times10^{-6}$	$1.700\pm0.008\times10^{-5}$	Taken during steam discharge of well

† Too much helium was present in the sample to obtain an accurate isotopic analysis.

COMPILATION OF QUESTIONNAIRE

During the Workshop, participants were asked to complete the questionnaire that appears on the following page and return it to the conveners by the end of the Discussion Session on Wednesday. The responses have been compiled by question and appear after the sample questionnaire. No attempt was made to prioritize the responses; they appear randomly as submitted.

QUESTIONNAIRE/WORKSHOP HOMEWORK
(Due after discussion session)

Name (Optional) _____

1. What, in your view, are the (few) most fundamental questions and problems discussed?

2. What are the key observable parameters which are needed to address them?

3. What methods or approaches are likely to yield important results?

4. What new methods and approaches are likely to be important (including: a) coordinated work on sample suites, b(continental drilling, c) measurements from space — remote sensing, telemetered data, etc.)?

5. Specific recommendations for future research programs or activities.

6. Has workshop been profitable? How could it have been improved?

1. What, in your view, are the (few) most fundamental questions and problems discussed?

A. Does the equilibrium observed in volcanic gases collected at the surface bear any relationship to the equilibrium of these gases in the melt?

B. Physico-chemical character(s) of supercritical volatiles

A. Volatile budget of the earth and understanding its relation to the origin and history of sea and air.

B. Understanding volcanic gases changes related to eruptions and/or intrusive events.

Questions — What is the exact composition of volcanic gases from different tectonic settings — see Fanale's list of questions

Problems — Need accurate, simple method for collection of volcanic gases in field — either continuous monitoring or periodic ; need accurate analysis of trace continuous and water abundances.

A. What is bulk composition of the Earth with respect to volatiles?

B. What are the outgassing ratios?

C. What is the gross flux of volatiles from earth? Net flux (source-sink) from earth? (What are the juvenile fluxes of all gases?)

D. What are key items for eruption prediction?

E. What is known about the solubility of volatile species in basalts especially f(P)

F. What is a reasonable working phenomenological model for a batch of Hawaiian magma?
- — How does it originate in mantle?
- — How does it migrate/interact?
- — What happens to it in the near-surface reservoir — interaction with walls, water, cooling, V

G. How different would subduction zone volcano be?

H. What could be done on gases in a deep drill hole?

A. Identification of juvenile volatiles and differentiation between juvenile and recycled volatiles.

B. Identification of one or a few chemical species which can be used as a reliable predictor of impending activity.

A. Volatile budget of earth: Is earth out-gassing or in-gassing?

B. Volatiles observed at surface: Juvenile or recycled?

Question 1 (continued)

A. Source (upper mantle)

A1. What are the amounts and concentrations of volatile components (C, O, H, S, N, Cl, F, P, Inerts) in the upper mantle?

A2. Are the volatile components distributed more or less uniformly, or are distributions inhomogenous?

A3. What are the stable phases and equilibrium distributions of the volatile components in source region (upper mantle)? That is, what is partitioning of the volatile components among stable mantle phases? This will require knowing at least the temperature, pressure and O_2 fugacity conditions for the upper mantle. How will volatile partitioning change as a function of these variables?

A4. What tools can we use to get the information for A1, A2, and A3? Mantle inclusions brought up in eruptions (perhaps meteorites) and geophysics seem to be about the only direct source of information.

B. Volatile input into and output from source (upper mantle)

B1. What are the amounts and rates of volatile transport into and out of the upper mantle?

B2. What are the mechanisms in each direction? What are the volatiles and their amounts carried in slabs down subduction zones? Do the volatiles stay with the slab, or do they outgas into the mantle surrounding the slab? Do gases percolate up from the mantle as a separate fluid phase or gas stream? Or, are gases piggy-backed up from the mantle only by transport in magmas? If the latter is the main method of transport, we need to know the solubilities for volatiles in magmas of different compositions. There is some solubility data for H_2O and CO_2, but there is little or none for S, Cl, F, N, and inerts.

C. Gas/Crust interactions

C1. Are volatiles from the crust commonly contaminating magmas as they pass through crust? By what mechanism do crustal volatiles get into magma — assimilation, convecting hydrothermal fluids, diffusion? Does magma remobilize crustal volatiles stored in old rocks?

C2. What is the nature of magma outgassing? At what depth does a gas phase develop? Does it occur by bubbles? How do bubbles form? Nucleation and kinetics of bubble formation? Does a gas form as a result of pressure drop, as a result of crystallization/differentiation, or both? How does the chemistry of the gas evolve as the magmas move upward, crystallize and differentiate? Do the outgassing fluids carry refratory components (SiO_2, Mg, Ca, Cu, Pb, Fe, Zn, etc.) with them and in what concentrations? How do these fluids interact chemically with the crustal host rocks — what are the product minerals, alteration assemblages, ore minerals deposited, etc?

C3. Do the gases play an important role in eruption of lava — i.e., do magmas get driven to an eruption mode because gases dissolved in them cause low density, or are magmas "pushed" out of the mantle and up through the crust by slugs of gas? We know something about the effects of volatiles on melt viscosity, but effects on melt density are not well known.

Question 1 (continued)

D. Interactions of magmatic gases with atmosphere, biosphere, hydrosphere.

A. What are the combustion processes occuring in volcanic flames? Is H_2 combustion the only process, or do other gases also contribute?

B. What are the details of gas exolution from melt in lava lakes and what is the relationship of this process to lake dynamics and thermodynamics?

C. What is the relationship of flames to fountain activity?

D. Are there primordial organic compounds in volcanic gas? Did volcanic gas in the prebiological atmosphere provide an input of complex organics?

E. What gases and isotopes of gases are useful to predict eruption at various types of volcanoes? (This is of great interest to me from the viewpoint of remote interrogation of in situ gas analysis on several volcanoes.

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2. What are the key observable parameters which are needed to address them?

Volatiles in rocks — qualitative and quantitative information

Volatiles erupted — qualitative and quantitative information

Flame spectra and flame photometry

A. Volatile inclusions in pheocrysts and the inter-relation between formation history and volatile components

B. All gas species should be studied for temporal changes

A. Measurement of temperature of gas and melt at collection site

B. Measurement of i) oxygen fugacity; ii) sulfur fugacity at collection site

C. Measurement of ratio of C:H:O:S species in gas

D. Halogen chemistry

Gas collection and analysis, glass inclusion and quenched rock analyses. Budget of volcanic products. Total analysis of altered ophiolites (what total composition is subducted?).

A. Compositions of volcanic gases as a function of time of eruption (e.g., pre-eruption, swelling, breakthrough, -flowing-, receeding, calm

B. Composition of gases at different sites, e.g., need analysis of gases from silica-rich volcanoes.

3. What methods or approaches are likely to yield important results?

A. Study of a well characterized suite of phenocrysts from differing environments

B. Study of wide ranging suite of fumaroles for all gas components above the present detection limits

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A. Collect high temperature volcanic gas collections with all techniques available (more important than low temperature sampling)

B. Studies of volatiles in trapped glass in phenocrysts (only technique for obtaining data on gases at depth for present)

C. Experimental studies of gas chemistry evolution as function of pressure (depth) and crystallization (Begin by getting solubility data for <u>all</u> volatiles.

Field studies — spectra

More experimental work

A. Study of volatiles in rocks (glass inclusions, etc.) and minerals a la Moore, Anderson, Gibson, Delaney, Munrow (?), Rose, etc.

B. Stable isotope chemistry of volatiles (H, C, S, N, ?) to trace reaction chemistry (assist in mass balance calculations, equilibria, etc.)

Geologic and oceanographic field work and sampling. Analytical work. Publication of data. <u>Interpretation</u> of data.

A. <u>In situ</u> measurements: i) Direct probes (e.g. H_2 probe) — in deep holes ii) continuous sampling, analyses, telemetry

B. Collection of equilibrium gases with non-contamination techniques

C. Continued analysis of phases which contain trapped equilibrium mixes of volcanic gases (e.g. phenocrysts)

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4. What <u>new</u> methods and approaches are likely to be important (including: a)coordinated work on sample suites, b)continental drilling, c) measurements from space — remote sensing, telemeterd data, etc.

A. Restoration techniques have the potential of providing accurate equilibrium composition data

B. Gas analysis of glass-phenocrysts must be continued, and detailed analysis must be undertaken to assess the potential for equilibrium composition.

Question 4 (continued)

Inexpensive, rugged instruments, easy to deploy are needed. Antennae that will work in snow, ice and storms also needed.

Remote sensing by spectrometer

A. Would instrumental deep bore hole measurements be important? Continental Drilling, Mauna Loa

B. What can be done from space?

C. Long term monitoring of key volcanoes

D. Should Pete Ward (in situ measurements, telemetered) by rejuvenated?

E. What has never been measured, which could be?

Studies of volatiles in trapped glass in phenocrysts.

"a" is the answer — a well chosen suite of good samples from different locations with analysis of all volatiles in matrix glass in phenocrysts and in inclusion glasses and a correlation with amount of glass (inclusion) which produces the volatiles.

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5. Specific recommendations for future research programs or activities.

A. inclusion fracture-gas analysis — high temperature, low temp., coordinated study of all volatiles.

B. Continued long term study of Kilauea and more explosive volcanic systems

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Continue monitoring established sites to develop methodology and equipment

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Instrument with simple seismic, tilt, temperature, and gas monitors 12 subduction volcanoes using satellite communications. Son of Peter Ward Experiment. NEEDS A HOME BASE.

Recommend expanding in situ probe and gas collection programs; develop a gas analysis lab at HVO which can be used by visiting investigators; expand spectral studies to include wider ranges — u.v. to far IR

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6. Has workshop been profitable? How could it have been improved?

Yes, longer and with a few more viewpoints represented.

Yes indeed. Would have been interesting to hear comments an experimental petrologist would have had on problems we discussed. I would have preferred

Question 6 (continued)

to have our final discussion after at least half a day to assimilate all that was said.

Needed talks on: origin of spectral features in gases — molecular, atomic
modern methods in molecular spectroscopy

Yes

Very

Yes!

Yes. Fred Anderson would have been most welcome.

Yes

Improvements: Permit longer papers — e.g. Reviews which can go into some depth - ∴ Extend meeting to 3 days

Invite someone similar to John Delaney who can talk about submarine basalt gases etc.

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APPENDIX

Table 1. Volatile inventory of the terrestrial planets

	α_i			x			r		
	V	E	M	V	E	M	V	E	M
N_2	0.034	0.78	0.027	1	~3	30 to 190	2.1×10^{-6}	2×10^{-6}	1.9×10^{-8} to 1.2×10^{-7}
CO_2	0.96	0.00033	0.953	1	$\sim 2 \times 10^{5}$	20 to 140	9.5×10^{-5}	7×10^{-5}	7.0×10^{-7} to 4.9×10^{-6}
H_2O	0.014	1×10^{-2}	1×10^{-3}	1	3×10^{4}	3×10^{5} to 2×10^{-6}	5.7×10^{-8}	1.6×10^{-4}	4.5×10^{-6} to 3.2×10^{-5}
Ne	4.3×10^{-6}	1.8×10^{-5}	2.5×10^{-6}	1	1	1	1.9×10^{-10}	1.1×10^{-11}	4.2×10^{-14}
Non-R Ar*	9×10^{-6}	4.0×10^{-5}	6.0×10^{-6}	1	1	1	8.1×10^{-10}	4.6×10^{-11}	2.2×10^{-13}
R Ar*	9×10^{-6}	9.3×10^{-3}	1.6×10^{-2}	1	1	1	8.1×10^{-10}	1.1×10^{-8}	5.4×10^{-10}

* Non-R Ar and R Ar mean nonradiogenic and radiogenic Ar (from ^{40}K decay), respectively. In the case of Venus we have assumed a 1/1 ratio of these components in deriving the α_i values, in accord with the Pioneer Venus mass spectrometer results.

α_i = measured mixing ratio of a given gas in the planetary atmospheres.

x = enhancement factor that takes account of the amount of given gas also present in any near-surface reservoir.

r = estimated ratio of the total mass of a given species to the planetary mass.

Table 2. Atmospheric composition of Venus as measured by the gas chromatograph.

Gas	Sample number		
	1	2	3
	*Concentration (%) ± confidence interval**		
CO_2	95.4 ± 20.1	95.9 ± 5.84	96.4 ± 1.03
N_2	4.60 ± 0.0880	3.54 ± 0.0261	3.41 ± 0.0207
H_2O	< 0.06	0.519 ± 0.684	0.135 ± 0.0149
	*Concentration (ppm) ± confidence interval**		
O_2	59.2 ± 25.2	65.6 ± 7.32	69.3 ± 1.27
Ar	30.3 + 46.9 - 20.3	28.3 ± 13.7	18.6 ± 2.37
Ne	< 8	10.6 + 31.6 - 9.6	4.31 + 5.54 - 3.91
SO_2	< 600	176 + 2000 - 0	186 + 349 - 156
Pressure (bars)	0.698 ± 0.140	2.91 ± 0.170	17.7 ± 0.183

* Confidence intervals are calculated from the calibration data acquired during the test and are determined to 3σ.

Tables are from Oyama V. I., G. C. Carle, F. Woeller, and J. B. Pollack (1979) Venus lower atsmopheric composition: analysis by gas chromatography. Science 203, 802-805.